

Kinetics of OH- and Cl-initiated oxidation of $\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$ and $\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$ and fate of the alkoxy radicals formed

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Abstract

Esters are emitted to the atmosphere in large quantities, either from natural or anthropogenic sources and are also formed by the oxidation of ethers. Esters are present in pheromones, fruits and essential oils, and they have pleasant odors, for these reasons are often added to consumer products to provide a pleasant odor (1). Unsaturated esters are also emitted from the industry, as vinyl butyrate that is used for synthetic production base materials in foods or beverages (2). Moreover allyl butyrate is widely used in the synthesis of polymers and copolymers as well as in the food industry as a flavoring (3, 4). Widespread use of the esters by industry inevitably results in fugitive emissions of the compounds to the atmosphere. Once in the atmosphere, these unsaturated esters, will be subjected to degradation through reaction with tropospheric oxidants, *i.e.*, mainly with OH radicals, NO₃ radicals, Cl atoms and O₃. Since the unsaturated esters will be mainly emitted in industrial centers and urban areas, their expected relatively fast reactions with tropospheric oxidants due to the presence of the double bond. In this study, rate coefficients of the reactions of OH and Cl radicals with vinyl and allyl butyrate were determined for the first time, the decay of the organics was followed using a gas chromatograph with a flame ionization detector (CG-FID) at 298 K and 1 atm using the relative method to be (in cm³ molecule⁻¹ s⁻¹): $k_1(\text{OH} + \text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.61 \pm 0.31) \times 10^{-11}$, $k_2(\text{Cl} + \text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.48 \pm 0.89) \times 10^{-10}$, $k_3(\text{OH} + \text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.89 \pm 0.31) \times 10^{-11}$, and $k_4(\text{Cl} + \text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.25 \pm 0.96) \times 10^{-10}$. Reactivity trends and atmospheric lifetimes of esters are presented. Additionally, a product study has shown the formation of butyric acid and polyfunctional compounds as products formed in the reactions of OH and Cl with vinyl and allyl butyrate. Atmospheric degradation mechanisms are proposed.

References

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